

## PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Rec'd PCT/PTO 22 MAR 2005

Applicant's or agent's file reference RJG/4087 WO	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB 03/04181	International filing date (day/month/year) 26.09.2003	Priority date (day/month/year) 26.09.2002
International Patent Classification (IPC) or both national classification and IPC B09C1/08		
Applicant UNIVERSITY OF BRIGHTON et al.		

<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 15 sheets.</p>
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I <input checked="" type="checkbox"/> Basis of the opinion</li> <li>II <input type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV <input type="checkbox"/> Lack of unity of invention</li> <li>V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI <input type="checkbox"/> Certain documents cited</li> <li>VII <input type="checkbox"/> Certain defects in the international application</li> <li>VIII <input type="checkbox"/> Certain observations on the international application</li> </ul>

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INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

International application No. PCT/GB 03/04181

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1-3 as originally filed  
4-16 received on 02.11.2004 with letter of 02.11.2004

**Claims, Numbers**

1-10 received on 02.11.2004 with letter of 02.11.2004

**Drawings, Sheets**

1/6-6/6 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

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5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-10
	No: Claims	
Inventive step (IS)	Yes: Claims	1-10
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-10
	No: Claims	

2. Citations and explanations

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

- D1: WO 97/28294 A (ELECTROCHEMICAL DESIGN ASSOCIA) 7 August 1997
- D2: US-B-6 221 2371 (LINDGREN ERIC R ET AL) 24 April 2001
- D3: WO 91/01392 A (IONEX ; GRAVES RICHARD (US); LOMASNEY HENRY L (US)) 7 February 1991

The document D1 is regarded as being the closest prior art to the subject-matter of claim 1, and shows an electrokinetic method for remediating soil comprising applying an electric field between electrodes implanted in soil whilst avoiding pH changes and precipitation of insoluble salts.

The subject-matter of claim 1 differs from this known method in that the electric current is applied such that an abrupt pH and Eh gradient is generated and that an iron rich band is precipitated.

The subject-matter of claim 1 is therefore new (Article 33(2) PCT).

The problem to be solved by the present invention may be regarded as the generation of a barrier to contaminant migration.

The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) since the cited prior art documents do not address the problem of creating an impermeable barrier by applying an electric field such that an abrupt pH and Eh gradient is generated.

Claims 2 to 10 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

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and up to 16% for licenses and other fixed costs (Ho *et al.*, 1997).

It is an object of the present invention to provide an improved electrokinetic method for groundwater protection, soil remediation and engineering which is low cost, efficient and flexible in its application. The

5 method involves:-

- the strategic and remote electrokinetic placement of an iron-rich barrier to a required geometry, which provides a physical and/or chemical barrier to contaminants, and improves the engineering properties of soils and sediments (contaminated or otherwise);
- 10 • the generation of a pH /Eh gradient to remobilise and/or trap contaminants within soils, sediments and slurries; and
- the stabilisation and strategic dewatering/rewatering of soils/sediments/slurries, the forced and directed migration of contaminated leachates, and the electro-osmotic purging of non-polar contaminants.

15 Unlike existing electrokinetic techniques, the method of the present invention provides a robust, non-selective and low energy approach to contaminant reduction and containment, and is based on natural iron mineralization processes that occur in the near-surface environment. In addition, since the system mimics nature (e.g. the formation of iron pans), and iron is a common major element in rock and soil systems and is relatively non-toxic, the environmental impacts are minimal. Moreover, iron itself has well-documented contaminant-trapping properties.

20 According to the present invention there is provided an electrokinetic method for groundwater protection, soil remediation and/or soil engineering which comprises applying an electric field between iron-rich sacrificial electrodes, which are implanted in an area of water-bearing soil, sediment or slurry, so as to generate an abrupt pH and Eh gradient from acid to alkaline conditions, with the spontaneous *in situ* precipitation of a stable iron-rich band occurring at the boundary between the acid and alkaline zones.

The method of this invention is characterised by increasing the mobility and solubility of contaminants through the application of an electric charge, and simultaneously arresting their migration either by fixation to an electrochemically-generated iron band which is precipitated 5 within the area under treatment, or via forced precipitation within the imposed Eh/pH field. This approach is distinct from other remediation techniques because it is geared towards deliberately producing an iron band *in situ* between the cathode and the anode, which simultaneously provides a physical as well as a chemical barrier; employs a low voltage of 10 typically less than 0.5 volts per cm distance between electrodes (with low energy requirements) to generate a strong Eh/pH gradient within soils and sediments; uses low cost, sacrificial cathode and anode materials; can produce, through differential dewatering, controlled differential subsidence 15 and permeability reduction; and which can be generated in natural and industrial materials over laboratory timescales. In contrast, current commercial techniques have an order of magnitude higher energy requirements, actively avoid generation of a pH gradient and precipitation of iron or contaminants within the soil or sediment (e.g. current electrokinetic techniques); or use *ex situ* clean-up/disposal; or hard 20 engineering technologies (e.g. permeable reactive barriers).

The present invention is a low voltage (< 0.5V/cm, in most cases less than 0.2V/cm) electro-chemical based technique, which uses electrokinetics to generate an intense pH gradient (typically from pH 2 – pH 13) and Eh gradient in soils, sediments and sludges, 25 destabilise/dissolve minerals and force the *in situ* precipitation of a stable iron-rich band. Internal electric fields of the scale used in the method of this invention commonly occur naturally in rock and soil bodies and can arise from a variety of conditions. A common result of this phenomenon is the electrical generation of bands of iron-stone in uncemented 30 sediments.(e.g. Jacob *et al.*, 1996). Such bands, which are found in many geological systems, can result when the electrolytic dissociation of water

takes place, with the formation of an anode zone characterised by acidic ions (pH 2.0 – 2.5), and a cathode zone characterised by alkaline ions (pH 10.5 – 11.5). As a consequence of the potential difference, a sharp boundary zone is developed within which an abrupt pH change from 2.5 to 5 8 occurs. Where sufficient iron is present in the system, spontaneous precipitation of insoluble metal (mainly iron) hydroxides and oxides occurs at the point of this pH "jump" (Jacob *et al.*, 1996). Small amounts of native (i.e. zero-valent) iron can also be present. In natural settings, such ferric iron-rich bands are commonly poorly crystalline or amorphous (e.g. 10 Hopkinson *et al.*, 1998).

The method of the present invention thus emulates these natural iron<sup>III</sup> mineralisation processes, but over experimental rather than geological timescales, by applying a direct electric potential to electrodes to grow bands of iron<sup>III</sup> mineral phases in sediment and soil columns, and to 15 harness their adsorptive properties, to trap or break down contaminants from the aqueous phase, or extracted from soil particles, during their migration in the applied electrokinetic field. Freshly precipitated amorphous or poorly crystalline Fe-rich solids, of the type generated by this method, are extremely effective scavengers of a range of heavy metals, 20 radionuclides and organic pollutants in a variety of environments (Bendell-Young and Harvey 1992, Cundy and Croudace 1995). Zero valent iron is itself an important catalyst for the dechlorination of toxic chlorinated aliphatic compounds (Haran *et al.*, 1996). Moreover, because this method generates strongly acidic conditions at the anode and strongly alkaline 25 conditions at the cathode, contaminants attached to soil or sediment particles (such as radionuclides and heavy metals), which are soluble under either acidic or basic conditions are solubilised and forced to migrate towards the appropriate electrode, whence they precipitate or are co-precipitated with the iron-band. In essence, the present invention provides 30 the opportunity to "flush" contaminants from parcels of contaminated sediments, and then retrap and concentrate them in, or adjacent to, the

iron-band. This offers the potential of *in situ* clean-up of contaminated soils, sediments and sludges. Clean-up of the whole soil volume between the electrodes can be achieved, and plating of contaminants onto the cathode avoided, by simply reversing the polarity of the electrodes at 5 regular intervals.

The approach embodied in the method of this invention is distinct from existing *in situ* remediation technologies, such as permeable reactive barriers, in that rather than merely sequestering contaminants from solution, the system actually mobilises contaminants into solution prior to 10 their subsequent trapping by the reactive band / imposed Eh/pH gradient, thus cleaning contaminated soils as well as ground waters. It differs from existing electrokinetic techniques in its use of low-cost electrodes (for example, electrodes made of cast iron, scrap iron, stainless steel or other iron-rich material), its low energy requirements and most significantly in its 15 deliberate generation of a sorptive iron-band in the material being treated. Hence, the electrokinetic technique described here is innovative and clearly distinguished from other electrokinetic treatment systems. The precipitated iron band, however, represents much more than merely a chemical sink for toxic contaminants liberated from the sediment column via oxidation- 20 reduction and pH reactions. The electrokinetic process that triggers iron band formation may also be used to improve the engineering properties, and massively reduce the permeability, of soils and sediments through differential dewatering of clays, and iron-band generation. Hence, electrokinetic ferric iron precipitation represents a means of physically 25 confining waste spills, providing a reactive barrier to liquid waste spillages that can be re-sealed and strengthened by periodic applications of electrical current (for instance in physically trapping and sorbing leachate that has percolated through the base liner of a landfill). In addition, the method offers the potential, through strategic dewatering or rewatering of 30 soils and sediments and iron-band generation, to rewater and stabilise soils for civil engineering applications (e.g. in building works). Existing

dewatering techniques involve complete dewatering of large-volume slurries (e.g. Lamont-Black 2001), whereas the present technique is applied *in situ* to strategically rewater or dewater, and strengthen or generally improve the engineering properties of, parcels of soil, and so has

5 a range of potential civil engineering applications (such as dealing with subsidence).

The method of this invention may have direct applicability in relation to the integrity of land fill liners, permeable reactive barrier technologies, and funnel and gate systems, controlled differential

10 subsidence, improving the engineering properties of soils and sediments, remediation of contaminated land (soils and sediments) and clean up of contaminated industrial sludges and slurries. Consequently, it will be of significant interest and potential benefit to a wide range of organisations, for example environment agencies, water companies, land fill operators,

15 civil engineering and environmental consultants and nuclear fuel companies.

The method of the present invention therefore has a number of surprising and significant benefits compared to other commercial techniques. In comparison with permeable reactive barrier technologies, it

20 provides a resealable iron-rich barrier, which can be remotely placed (without engineering) at working sites and sites with infrastructure to physically and chemically inhibit subsurface pollutant migration, and can redirect subsurface pollutant flow. In comparison with commercial electrokinetic remediation techniques it has an order of magnitude lower

25 energy requirements and electrode cost, does not involve the use of potentially toxic conditioning solutions, can remobilise contaminants from the solid phase and simultaneously trap and contain contaminants in the liquid phase, and can be applied on working sites, or sites containing infrastructure.

30 The low voltage used, coupled with the flexibility provided by the use of multiple, low cost electrodes, means that contaminated land can

be sequentially treated with a series of electrode arrays, whereby the distance between individual electrodes does not exceed a few metres. In addition, the current is sufficiently low to avoid soil heating and large-scale gas generation at the electrodes. Adjustable electrode geometry means 5 that the technique can be adapted to suit site-specific conditions, and large areas of land can be sequentially treated. It will be appreciated that the iron may be precipitated to form an impermeable coherent band, or a coating which cements soil/sediment particles, or a dispersed coating on mineral grains, between two or more electrodes. Following treatment, the 10 iron band can simply be excavated as a coherent mass, or left *in situ* to provide a long-term inert, and, via reapplication of current, resealable barrier.

15 The method of this invention provides an *in-situ*, sustainable, cost-effective electrokinetic technology for groundwater protection and soil remediation, which can be operated in combination with, or as an alternative to, existing land remediation technologies. The technique is applicable to small sites, as well as larger areas of contaminated land, and can be implemented in ground where man-made structures are present, or where there is on-going site activity.

20 The method of this invention will now be illustrated by the following examples and the accompanying drawings:-

Figure 1 shows a sub-vertical, 1cm thick Fe-rich band generated in water-saturated sands after 30 hours application of a 1.5V potential difference between cast iron electrodes.

25 Figure 2a shows the generation of an Fe band in clay soil medium using the method of the present invention.

Figure 2b shows a diatom (marine microorganism) which, together with the underlying silt particle, has been coated and cemented by iron using the technology outlined in this application.

30 Figures 3a – d relate to data from a hydrocarbon purging experiment, using spiked Southampton Water mud. Figure 3a shows mid

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IR spectrum for original engine oil used for spiking the sediment. Figures 3b, c and d show FT-IR spectra for effluent drained from the cathode compartment on days 5, 12 and 13 respectively of the experiment. Note the hydrocarbon and seawater absorption lines are marked. Note also the

5 number of FT-IR active diesel lines, and their overall intensity, increases with experimental time (e.g. day 13 CH<sub>3</sub> bend at 1376.66 cm<sup>-1</sup>, appears). This indicates that the diesel within the cathode zone effluent became increasingly concentrated with experimental time.

Figures 4a and b show <sup>60</sup>Co and As data for treated Ravenglass 10 estuary mud. Fe band is located 5cm from the anode. Note change in y-axis units, with <sup>60</sup>Co in Bq/g (or atomic disintegrations per second per gram) and As in ppm. Error bars on As data are smaller than the diamond marker symbol used. Note ca. ~40 % reduction of As in cathodic compartment, and ~100 % enrichment in narrow iron band. Reduction in 15 <sup>60</sup>Co is less notable, but still exceeds 30 % in the anode zone (compared to the untreated material). A ~50 % enrichment in the iron band compared to untreated material (which corresponds to a ~110 % enrichment in <sup>60</sup>Co over the anode zone) is also observed.

20 Examples

Pilot studies have been applied at laboratory scales in 25 x 2 x 15cm and 30 x 50 x 40cm open topped perspex cells (i.e. effectively in two dimensional and three dimensional space). All experiments have been run at <5 volts, using sacrificial cast iron 25 electrodes. Electrodes were fabricated from 25mm diameter cast iron rods (Grade 250), composition: C 3.48%, Si 2.87%, Mn 0.812%, S 0.099%, P 0.364%, Fe REM. Experiments have been run on a variety of contaminated muds, with groundwater and seawater interstitial pore waters, under unsaturated and saturated conditions. Time scales range 30 from 3 to 400 hours.

In experiments using sand, the initial permeability of the

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sands was  $0.48 \times 10^{-5}$  m/s, post -treatment permeability (in the iron band) was recorded at  $0.19 \times 10^{-5}$  m/s. For the mud experiments, initial permeability was typically  $-0.29 \times 10^{-7}$ , whereas treated material permeability (in the iron band) was recorded at  $10^{-9}$ , or less, i.e. practically 5 impervious. In addition, clear dewatering was consistently observed in the sediment around the anode, and rewatering around the cathode.

In every case, a strongly acidic zone was generated around the anode (approx. pH 2), and an alkaline zone around the cathode (approx. pH 13). At the point of abrupt pH change, approximately 10 equidistant between cathode and anode, a 1 - 4cm thick, coherent, iron stone was precipitated (Figure 1) having an approximate uniaxial compressive strength comparable to a moderately lithified sandstone (or the strongest Chalks in southern England). The iron stone generated 15 consists of an amorphous iron band (see Figure 2a), or, in sandy sediments, a coating of zero valent iron and iron oxides which cement mineral grains. The presence of zero valent iron in the Fe-rich band is noteworthy since a large proportion of permeable reactive barriers employed at contaminated sites are based on the use of zero-valent iron to 20 act as a powerful chemical reductant for chlorinated aliphatic compounds dissolved in groundwater (Younger, 2002). It is also possible to rapidly generate a dispersed sorptive coating of iron on a pre-defined area of soil 25 without significant loss of porosity, simply by switching off the current before the Fe- band fully develops (Figure 2b). Such an approach may be desirable in situations where the sorptive properties of iron can be harnessed to reduce the concentration of specific contaminants, such as arsenic (As), in groundwater.

Two specific studies are now presented which illustrate the applicability and potential of the method of the present invention for containing leachate and dissolved phase contaminants and remediating 30 contaminated land.

1. Hydrocarbon and heavy metal contaminated sediments,

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Southampton Water

A) An estuarine mud sample, contaminated with copper (Cu) and petroleum hydrocarbons from the nearby Fawley oil refinery and from discharges from local shipping, was treated using a voltage of 2 V, in a 5 three-dimensional cell using a rectangular electrode array. A continuous iron band of up to 3 cm thickness was generated from the electrode point sources. Data for pre- and post-treatment Cu concentration indicate that the electrokinetic treatment resulted in an approximate reduction of 61 % in Cu contamination in the anode zone in 16.3 days (note that a small 10 proportion of Cu is natural background Cu held within the crystal lattice of stable minerals. This naturally occurring Cu is not influenced by the electrokinetic process). Notably, liquid hydrocarbon-rich effluent was expelled from the sediment (via electro-osmotic purging) and channeled and drained at approximately 10 ml per day from the surface of the 15 cathodic compartment. The energy requirement for the experiment was 10.9 kW/m<sup>3</sup>. These values compare favourably against commonly cited energy requirements for other electrokinetic remediation systems, e.g. 500 kW/m<sup>3</sup> for 100 % removal of metal contaminants (Virkutyle *et al.*, 2002). The timescale for copper decontamination and hydrocarbon purging 20 from the sediment is comparable in duration to existing technologies which employ comparatively expensive cation-selective membranes (Van Cauwenbergh, 1997). The use of cast iron electrodes (as opposed to gold coated, platinum or graphite electrodes), means that the experimental system is low cost in terms of energy, materials and electrode construction, 25 which typically make up ~70 % of the costs associated with any electrokinetic remediation system (Ho *et al.*, 1997).

B) To examine hydrocarbon decontamination by the method of the present invention, a sample of seawater saturated Solent mud was spiked with 0.4 litre of fresh 15W/40 (Halfords) engine oil, and treated at 2V 30 for 13 days. Small volumes of clean seawater were added around the anode electrodes to prevent desiccation of the sediment. Effluent was

removed intermittently by pipette from a 1cm deep trench dug in the cathode compartment. The effluent samples were analysed via Fourier Transform mid-infrared (FT-IR) spectroscopy. The resultant FT-IR spectra clearly show the hydrocarbon-rich nature of the effluent (i.e. the output solution) compared to the clean seawater added (i.e. the input solution).  
5 Essentially, the hydrocarbons (in this case engine oil) contained in the clay-rich sediment are extruded or purged via an electro-osmotic flow of water from the anode to the cathode, and replaced by clean seawater. (Figure 3a – d).

10 The natural moisture content of the untreated sediment was 97%, compared to 69% and 88% for the anode and cathode zones respectively, consistent with the extraction of purged hydrocarbon-rich effluent from the cathode zone, and electro-osmotic flow of water from the anode to cathode zone. The bulk density of the cathode zone was recorded  
15 at 1.47 Mg/m<sup>3</sup> (wet), 0.78Mg/m<sup>3</sup> (dry), specific gravity 2.59. Anode zone bulk density was recorded at 1.49/m<sup>3</sup> (wet), and 0.88 Mg/m<sup>3</sup> (dry), specific gravity 2.62. These differences in physical properties between the anodic and cathodic zone are consistent with the addition of iron to anodic zone sediment, during the experiment. The hand Vane shear strength of the  
20 anode sediments is 2.45 K Pa , compared to zero for cathode zone and untreated sediment. This indicates a significant improvement in the engineering properties of the anode zone sediments as a consequence of electro-osmotic dewatering, accompanied by precipitation.

2. Radioactively-contaminated sediment, Ravenglass, Cumbria

25 A clay-rich sediment sample, slightly contaminated with artificial radionuclides, was collected from the Ravenglass estuary, Cumbria and treated at 1.5 V for 410 hours in a two-dimensional perspex cell, using an electrode separation of 17 cm. A 17 mm thick Fe-rich band was generated 5 cm from the anode, at the point where a major step in pH  
30 (from pH 2 to pH 13) occurred. Geochemical and radiometric analysis of the treated sediment (see Figure 4) shows clear removal of radioactive

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cobalt ( $^{60}\text{Co}$ ) from the anode zone of the cell, and precipitation of the remobilised  $^{60}\text{Co}$  on the iron-rich band. This was achieved in a short 17 day timescale compared with commercial systems which typically operate over durations of 20 -100 days.

5       Manganese (Mn), calcium (Ca) and strontium (Sr) were also remobilised from the anode zone and precipitated on, or around, the iron band. Soluble ions such as iodine (I), bromine (Br) and sodium (Na) migrated towards the appropriately charged electrode. Notably, As, present as a trace contaminant in these sediments, was highly amenable to  
10      the treatment, with desorption occurring at high pHs in the cathode zone. A 100 % enrichment of As occurred on the iron-rich band (see Figure 4), reflecting the strong affinity of As for the amorphous precipitated Fe. The highly particle-reactive radionuclides plutonium (Pu) and americium (Am), present at elevated activities in this sediment, were not significantly  
15      remobilised over the timescales used. The method of the present invention, however, can still be used to contain leachates contaminated with these radionuclides due to the action of the Fe band as a barrier to groundwater flow, the strong association of Pu and Am with freshly precipitated amorphous iron oxide phases, and the action of the applied  
20      electric field, which forces ionic and colloidal species to migrate towards the appropriately charged electrode.

25      In summary, unlike existing electrokinetic techniques which actively avoid precipitation of minerals and salts in the soil mass between the two electrodes, the method of the present invention is specifically geared towards producing an iron-rich band *in situ* between cathode and anode. This iron band simultaneously provides a physical as well as a chemical barrier to leachate migration. The method also employs a low voltage (with low energy requirements) to generate a strong pH gradient within soils and sediments and can desorb a range of polar and ionic  
30      contaminants. It uses low cost, sacrificial cathode and anode materials, and can produce, through differential dewatering, water movement and

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electro-osmotic purging of non-polar organic contaminants.

## REFERENCES

- 5 1. Acar Y.B, Alshawabkeh A.N (1993) Environmental Science and Technology **27**, (13) 2638-2647.
- 10 2. Bendell-Young L, Harvey H.H (1992) Geochim.Cosmochim.Acta **56**, 1175-1186.
- 15 3. Cundy A.B. and Croudace I.W. (1995) Journal of Environmental Radioactivity **29**, 191-211.
4. Haran B.S., Popor B.N, Zheng G, White R.E., (1996), Environ Prog **15** (3), 166 – 172.
5. Ho S.V, Athmer C.H, Sheridan P.W, Shapiro A.P. (1997) Journal of Hazardous Material **55**, 39-60.
- 20 6. Ho S.V, Athmer C.H, Sheridan PW, Hughes BM, Orth R. McKenzie D, Brodsky P.H, Shapiro A.P, Thornton R, Salvo J, Schultz D, Landis R, Griffith R, Shoemaker S, (1999) Environmental Science and Technology, **33**, 1086-1091.
- 25 7. Hopkinson L, Roberts S, Herrington R, Wilkinson J (1998) Geology **26**, 347-350.
8. Jacob K-H, Dietrich S, Krug H-J (1996) Self organised mineral fabrics. In: Kruhl J.H, Fractals and dynamic systems in geoscience. Springer Verlag, Berlin, 259-268.

- 16 -

9. Kovalick W.W. (1995) In situ remediation technology: electro-kinetics. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response Technology Innovation Office, Washington, EPA542-K-94-007.
- 5  
10. Lageman R (1993) Environmental Science and Technology, 27 (13) 2648-2650.
11. Lamont-Black J (2001) Ground Engineering 34, 22-23.
- 10  
12. Van Cauwenberghe (1997) Electrokinetics: Technology overview report. Groundwater Remediation Technologies Analysis Centre, 1-17.
- 15  
13. Virkutyte J, Sillanpaa M, Latostenmaa P (2002) The Science of the Total Environment 289, 97-121.
14. Younger P. (2002), CL:AIRE view, Autumn 2002.

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CLAIMS

1. An electrokinetic method for groundwater protection, soil remediation and/or soil engineering which comprises applying an electric field between iron-rich sacrificial electrodes, which are implanted in an area of water-bearing soil, sediment or slurry, so as to generate an abrupt pH and Eh gradient from acid to alkaline conditions, with the spontaneous *in situ* precipitation of a stable iron-rich band occurring at the boundary between the acid and alkaline zones.
- 10 2. A method as claimed in claim 1, wherein the pH gradient is from pH2 to pH13.
3. A method as claimed in claim 1 or claim 2, wherein the current is applied between one or more pairs of electrodes inserted in the area of soil, sediment or slurry.
- 15 4. A method as claimed in claim 3, wherein the electrodes are made of cast iron, scrap iron, stainless steel or other iron-rich material.
5. A method as claimed in claim 3 or claim 4, wherein the voltage employed is less than 0.5 volts per cm of the distance between a pair of electrodes.
- 20 6. A method as claimed in any one of the preceding claims, wherein the soil, sediment or slurry contains organic, inorganic and/or radioactive contaminants.
7. A method as claimed in any one of the preceding claims, wherein the iron-rich band acts as a physical and/or chemical barrier to contaminants present in the soil, sediment or slurry.
- 25 8. A method as claimed in any one of the preceding claims, where iron is precipitated to form an impermeable coherent band, or a coating which cements soil/sediment particles, or a dispersed coating on mineral grains, between two or more electrodes.
- 30 9. A method as claimed in any one of the preceding claims, wherein the generation of the pH / Eh gradient mobilises, remobilises

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and/or traps contaminants present in the soil, sediment or slurry.

10. A method as claimed in any one of the preceding claims,  
which is performed for the purpose of the stabilisation and/or strategic  
dewatering/rewatering of soils, sediment and/or slurries, the improvement  
5 of the physical properties of soils and sediments for engineering purposes,  
the forced and directed migration of contaminated leachates, and/or  
electro-osmotic purging of non-polar contaminants.